

# Stochastic processes: Measuring diffusion

— Shanghai, 1st July 2018 —

# The bromine experiment



# Relaxation processes

Deborah number:

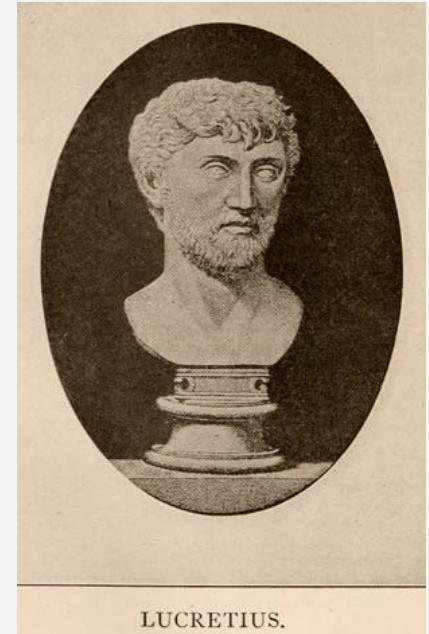
$$\tau = \frac{\text{Relaxation time scale}}{\text{Experimental time}}$$

The tar pitch drop experiment (U Queensland):

Date	Event
1927	Setup experiment
1930	Stem cut
12/1938	1st drop fell
02/1947	2nd drop fell
04/1954	3rd drop fell
05/1962	4th drop fell
08/1970	5th drop fell
04/1979	6th drop fell
07/1988	7th drop fell
11/2000	8th drop fell



*. . . for behold whenever  
The sun's light and the rays, let in, pour down  
Across dark halls of houses: thou wilt see  
The many mites in many a manner mixed  
Amid a void in the very light of the rays,  
And battling on, as in eternal strife,  
And in battalions contending without halt,  
In meetings, partings, harried up and down.*

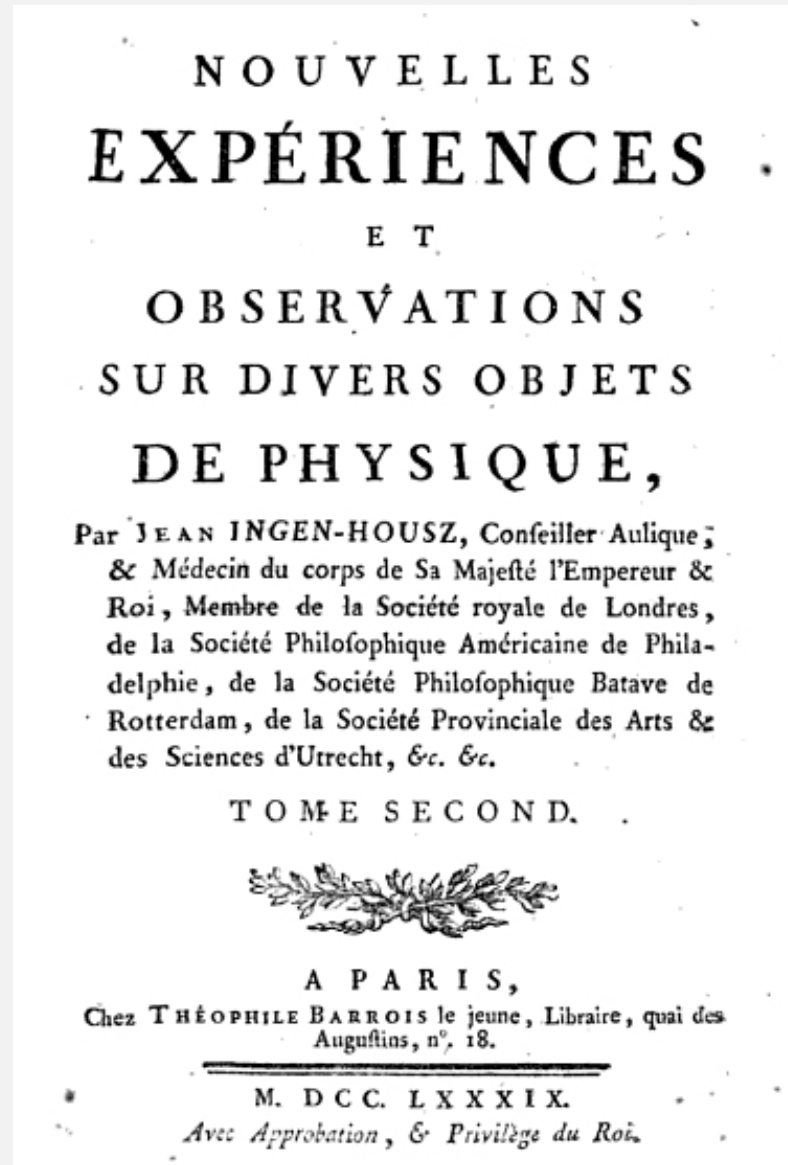


*Laß in ein dunkles Zimmer einmal die Strahlen der Sonne  
Fallen durch irgendein Loch und betrachte dann näher den Lichtstrahl:  
Du wirst dann in dem Strahl unzählige, winzige Stäubchen  
Wimmeln sehn, die im Leeren sich mannigfach kreuzend vermischen,  
Die wie in ewigem Kriege sich Schlachten und Kämpfe zu liefern  
Rottenweise bemühen und keinen Moment sich verschnaufen.  
Immer erregt sie der Drang zur Trennung wie zur Verbindung.*

On the Nature of Things, Titus Lucretius Carus (50 BCE)

# Dutch physician Jan Ingenhousz 1785

Described the jittery motion of coal dust on an alcohol surface



This plant was *Clarkia pulchella*, of which the grains of pollen, taken from antherae full grown, but before bursting, were filled with particles or granules of unusually large size, varying from nearly 1/4000th to 1/5000th of an inch in length, and of a figure between cylindrical and oblong, perhaps slightly flattened, and having rounded and equal extremities. While examining the form of these particles immersed in water, I observed many of them very evidently in motion; their motion consisting not only of a change of place in the fluid, manifested by alterations in their relative positions, but also not unfrequently of a change of form in the particle itself; a contraction or curvature taking place repeatedly about the middle of one side, accompanied by a corresponding swelling or convexity on the opposite side of the particle. In a few instances the particle was seen to turn on its longer axis. These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself.—1828



## Microscopical observations

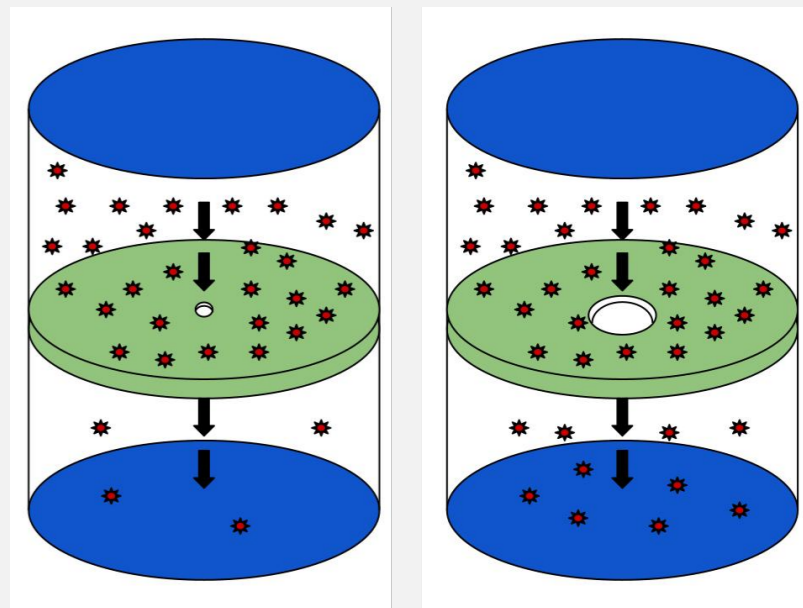
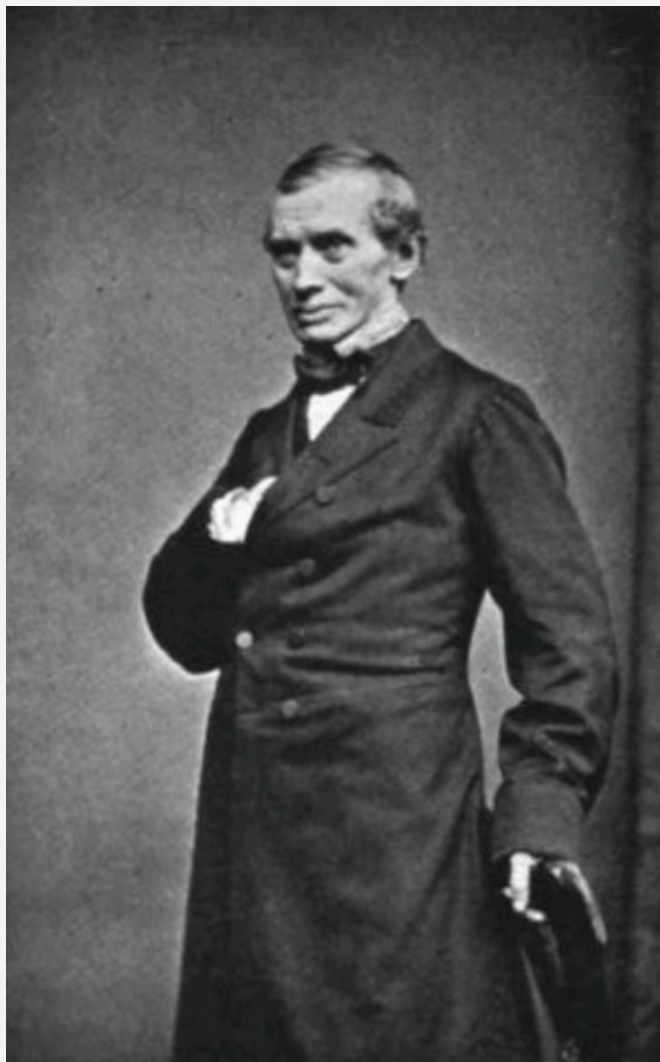
on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies

Rocks of all ages, including those in which organic remains have never been found, yielded the molecules in abundance. Their existence was ascertained in each of the constituent molecules of granite, a fragment of the Sphinx being one of the specimens examined.



# Scottish chemist Thomas Graham 1846

Formulates a law of effusion of gases



Effusion (left) vs diffusion (right)

Graham's law:

$$\frac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} = \sqrt{\frac{M_2}{M_1}}$$

$M_i$ : molecular mass



# Jean Perrin



Scanned at the American  
Institute of Physics



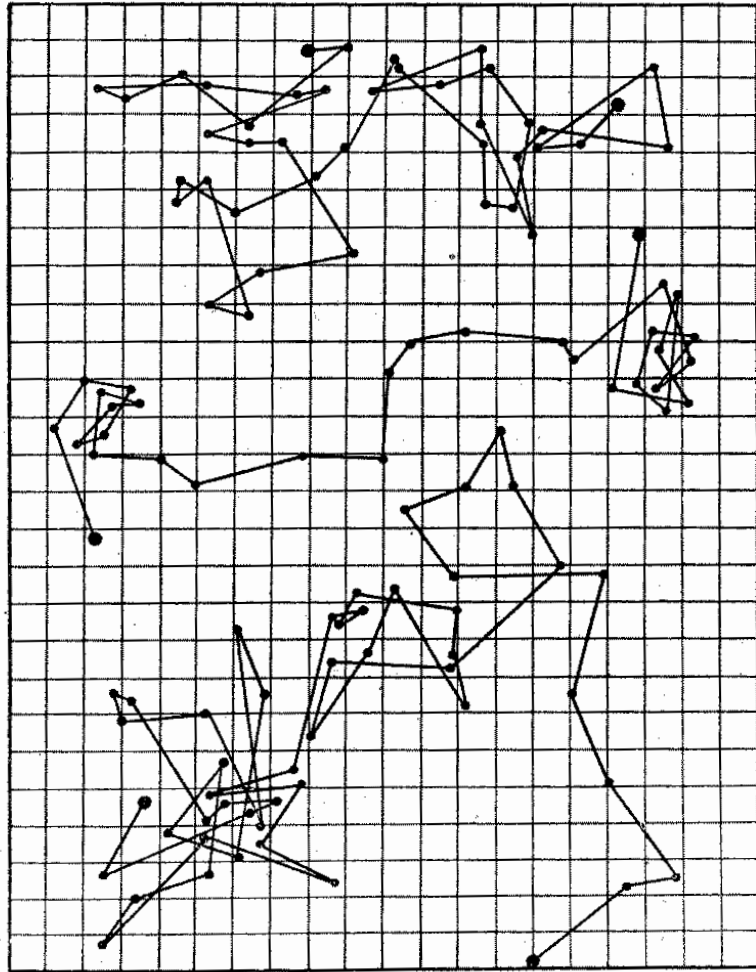
Scanned at the American  
Institute of Physics



Scanned at the American  
Institute of Physics

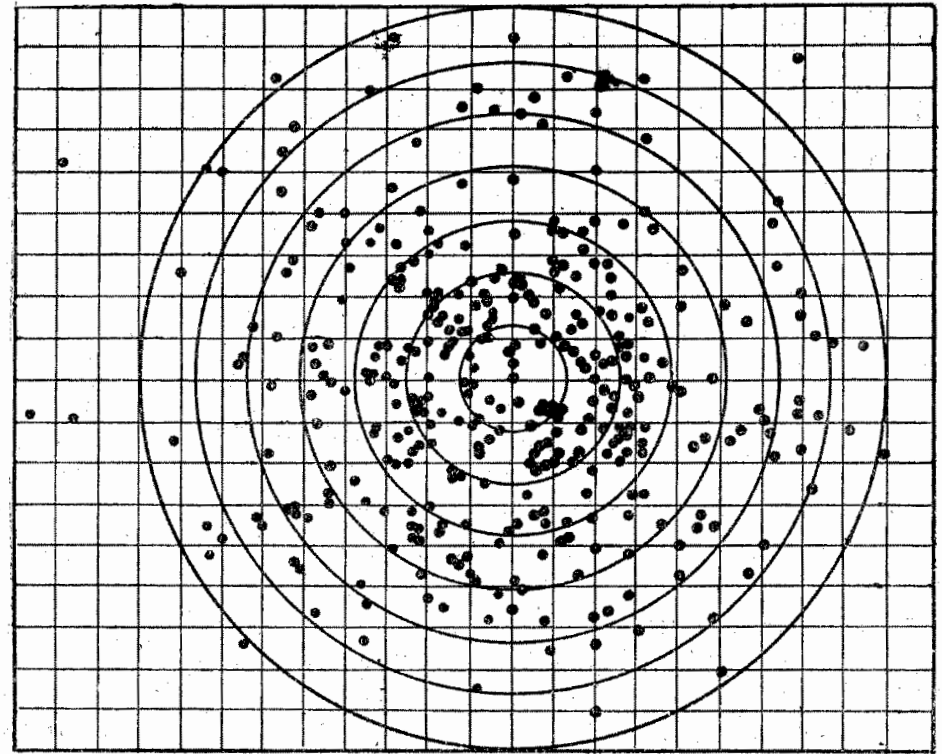
# Brownian motion

Fig. 6.



$\Delta t = 30 \text{ sec}$

Fig. 7.

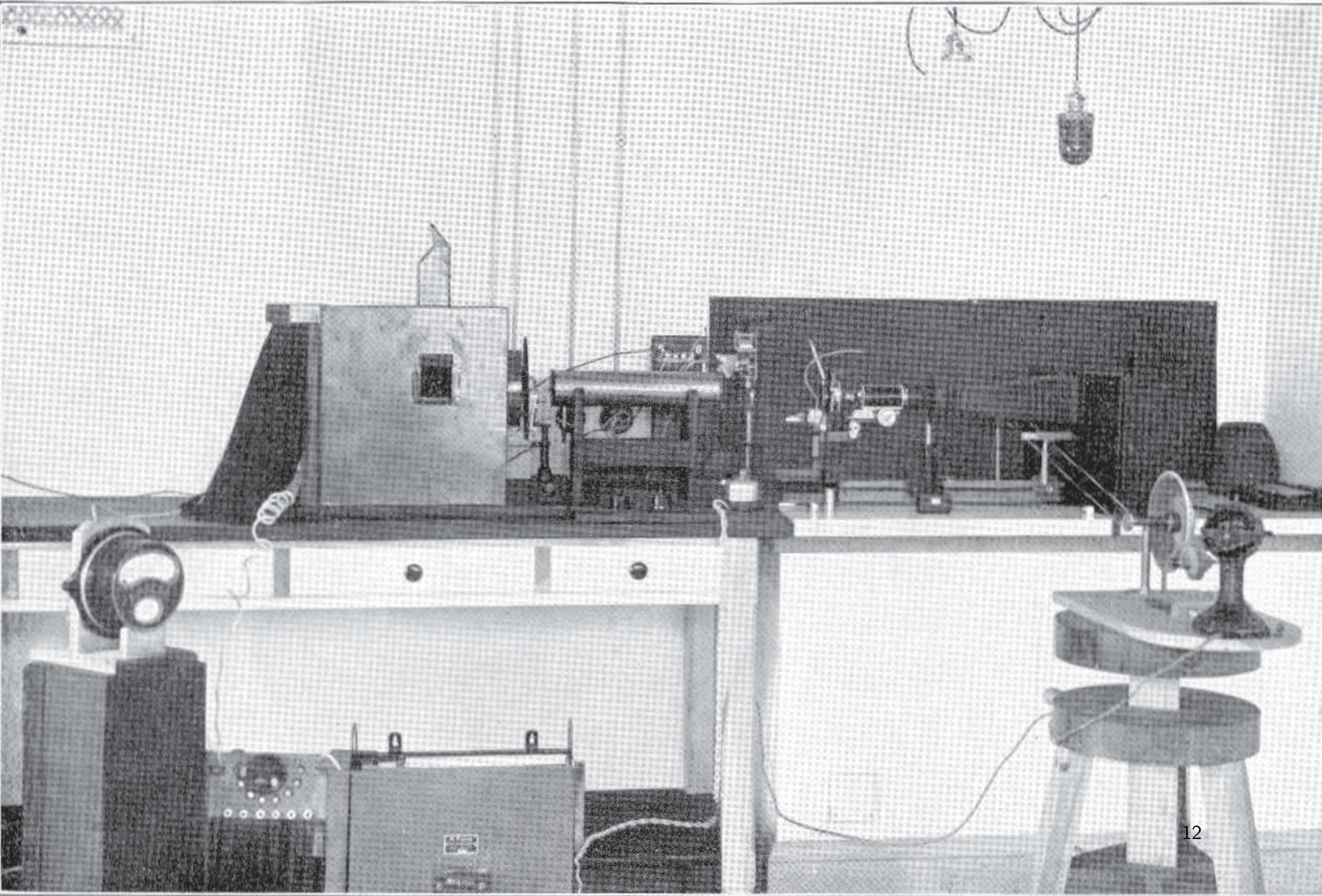


$$P(\mathbf{r}, \Delta t) = \frac{1}{(4\pi K \Delta t)^{d/2}} \exp\left(-\frac{r^2}{4K \Delta t}\right)$$

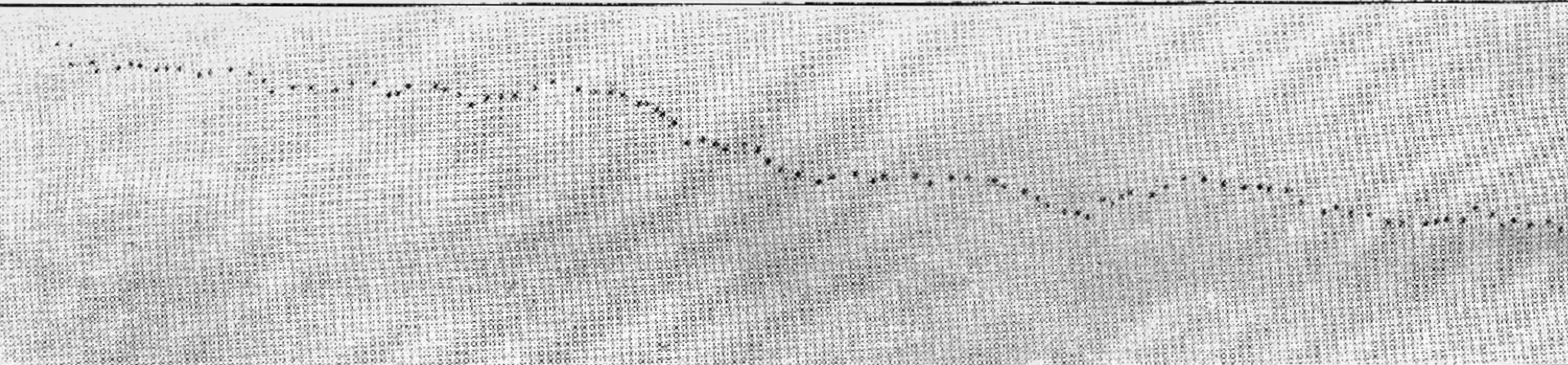
Einstein-Smoluchowski relation:

$$K = \frac{k_B T}{m\eta} = \frac{(R/N_A)T}{m\eta}$$





# Ivar Nordlund: 100 years of SPT with time series analysis



Mercury droplet in aqueous solution

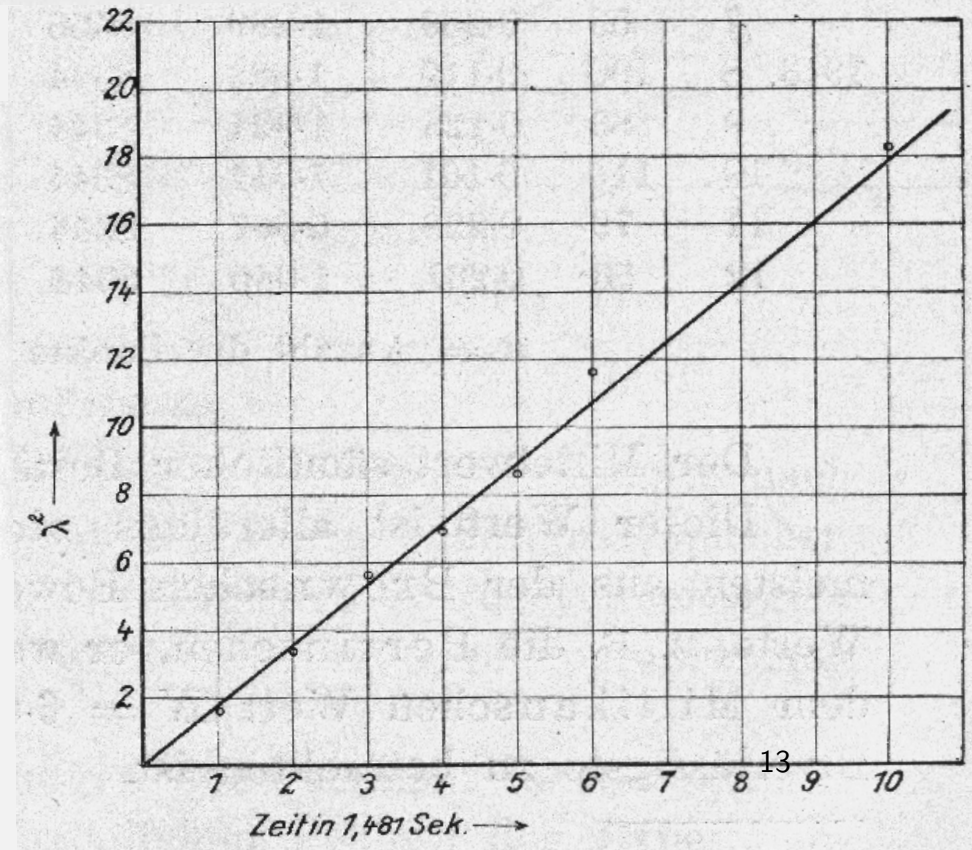
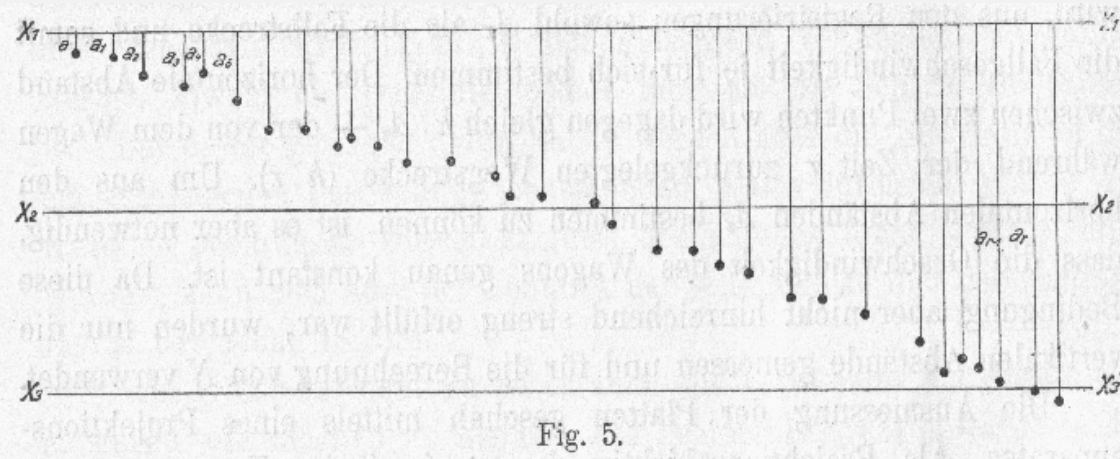


Fig. 11.

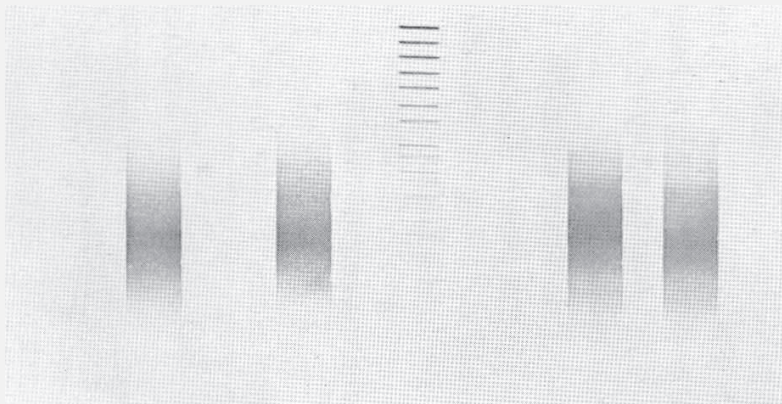
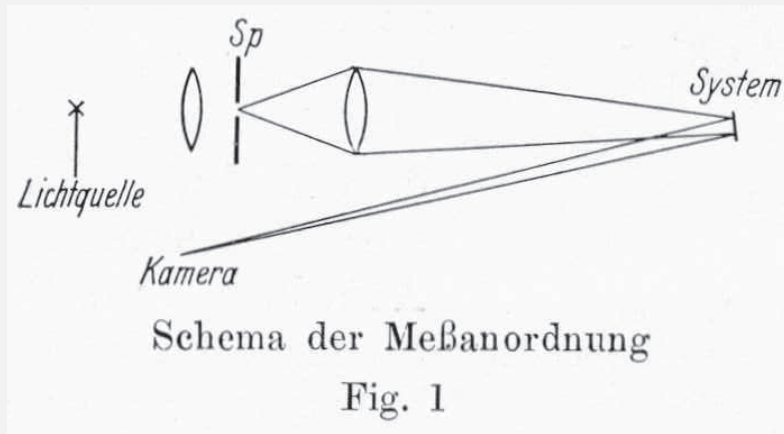
I Nordlund, Z Physik (1914):  $N_A = 5.91 \times 10^{23}$

# Eugen Kappler: ultimate diffusion measurements

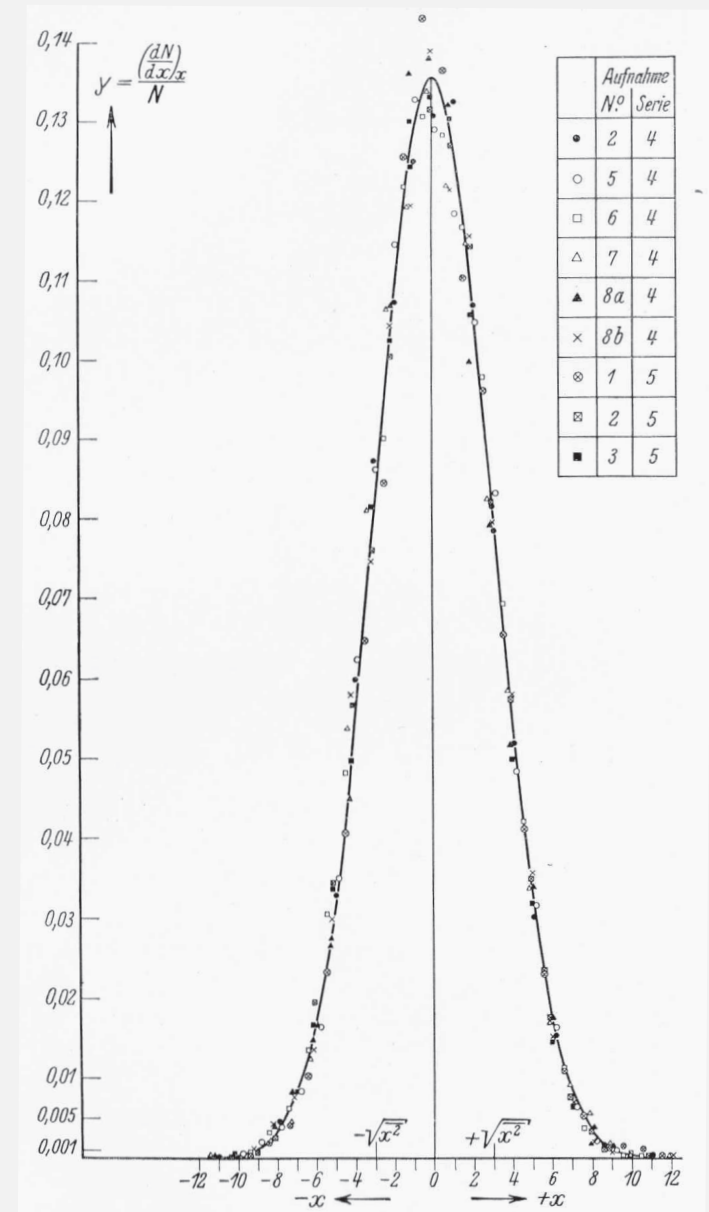


Obituary by L Reimer, Physikalische Blätter Feb 1978 pp 86

# Eugen Kappler: ultimate diffusion measurements

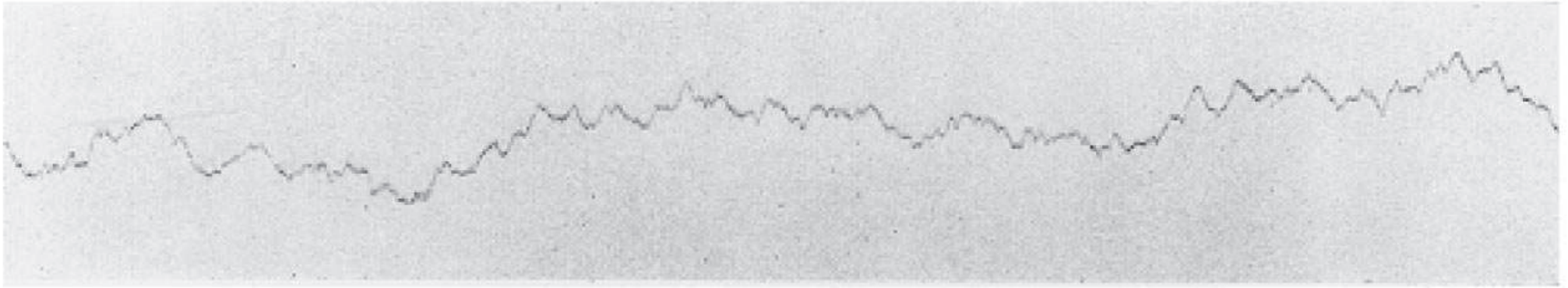


Distribution @ fixed photographic plate



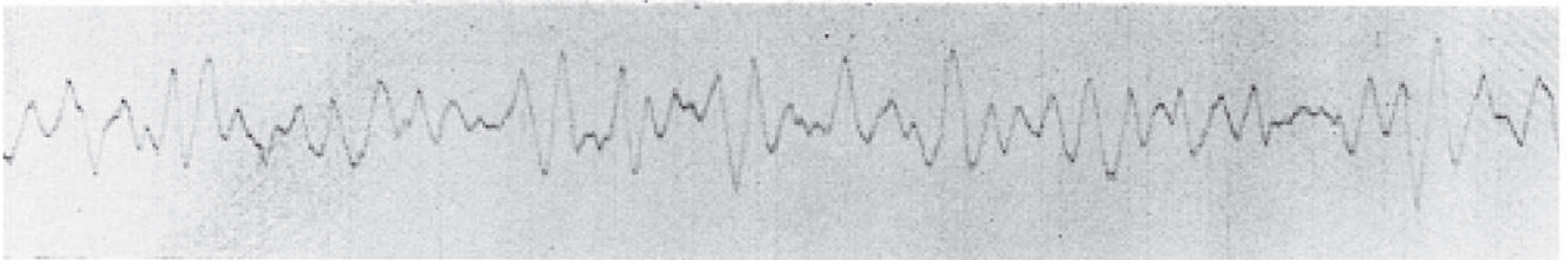
E Kappler, Ann d Physik (1931):  $N_A = 60.59 \times 10^{22} \pm 1\%$

# Eugen Kappler: ultimate diffusion measurements



Registrieraufnahme der Brownschen Bewegung (natürliche Größe).  
Direktionskraft  $9,428 \cdot 10^{-9}$  abs. Einh. Trägheitsmoment:  $1 \cdot 10^{-7}$  abs. Einh. Abstand Spiegel-Kamera: 72,1 cm.  
Zeitmarke: 30 sec  $dx = 1$  mm. a) Atmosphärendruck. Temperatur  $13^{\circ}$  C

Fig. 5 a



Registrieraufnahme der Brownschen Bewegung (natürliche Größe).  
Direktionskraft  $9,428 \cdot 10^{-9}$  abs. Einh. Trägheitsmoment  $1 \cdot 10^{-7}$  abs. Einh. Abstand Spiegel-Kamera: 72,1 cm.  
Zeitmarke: 30 sec  $dx = 1$  mm. b)  $1 \cdot 10^{-8}$  mm Hg. Temperatur  $13^{\circ}$  C

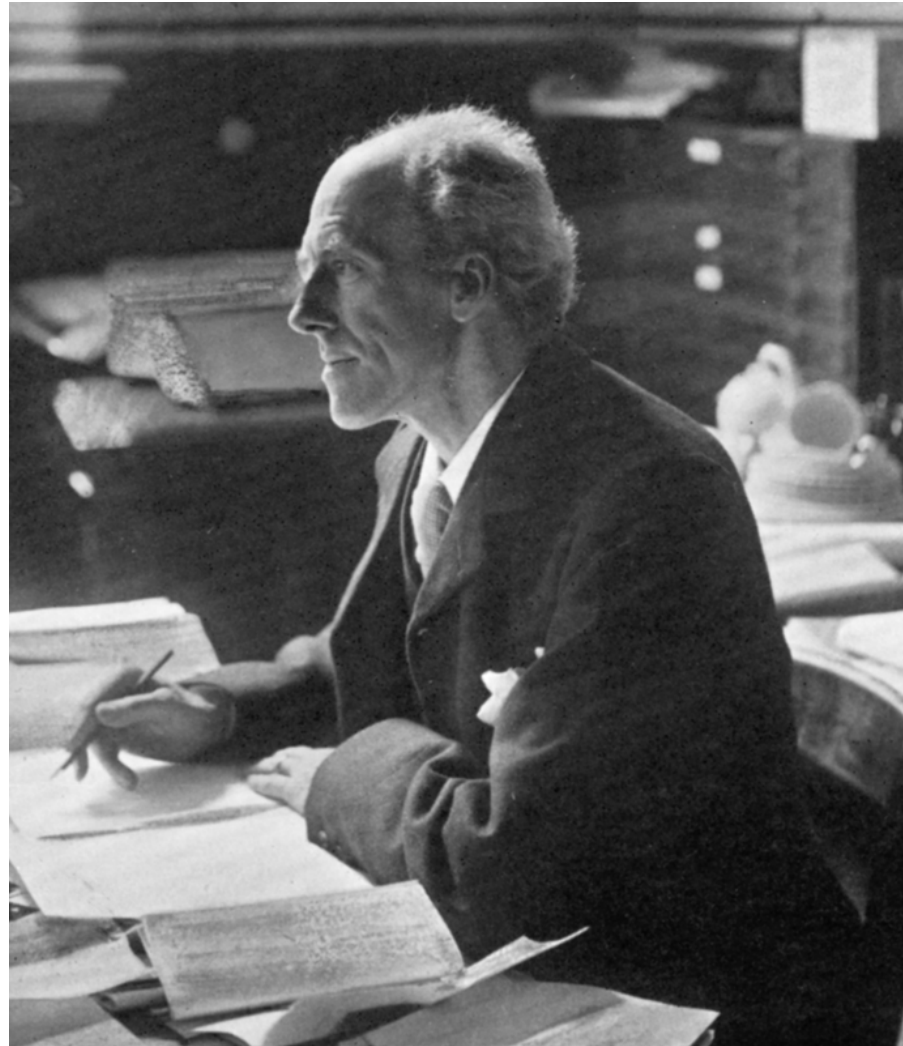
Fig. 5 b



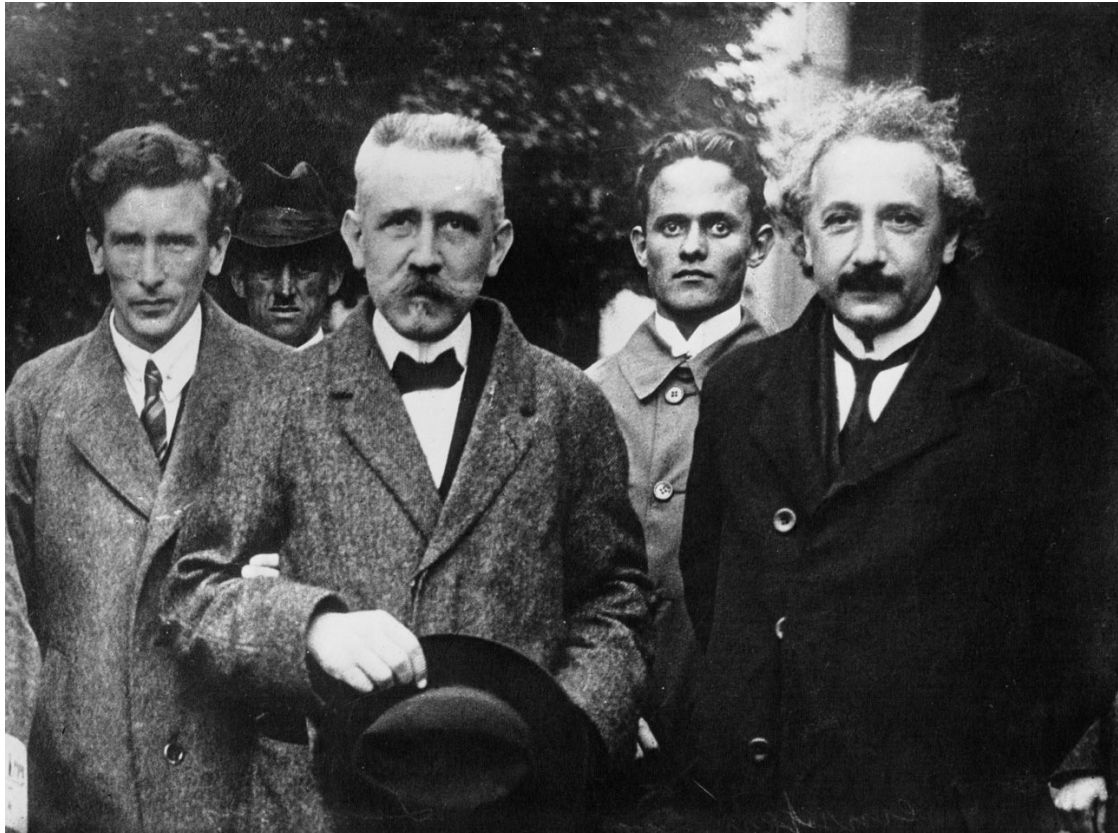
## Enter the theorists...



Adolf Fick



Karl Pearson



Paul Langevin & Albert Einstein



Marian Smoluchowski



William Sutherland

1904 paper on diffusion presented at Dunedin ANZAAS conference

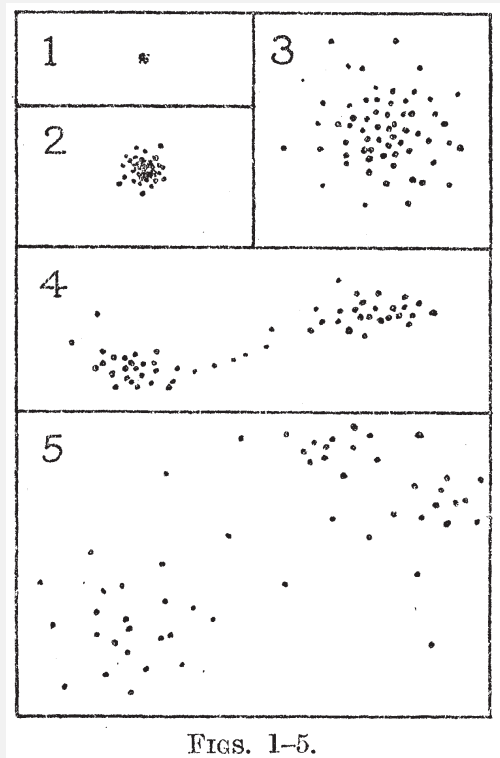


Lewis Frey Richardson

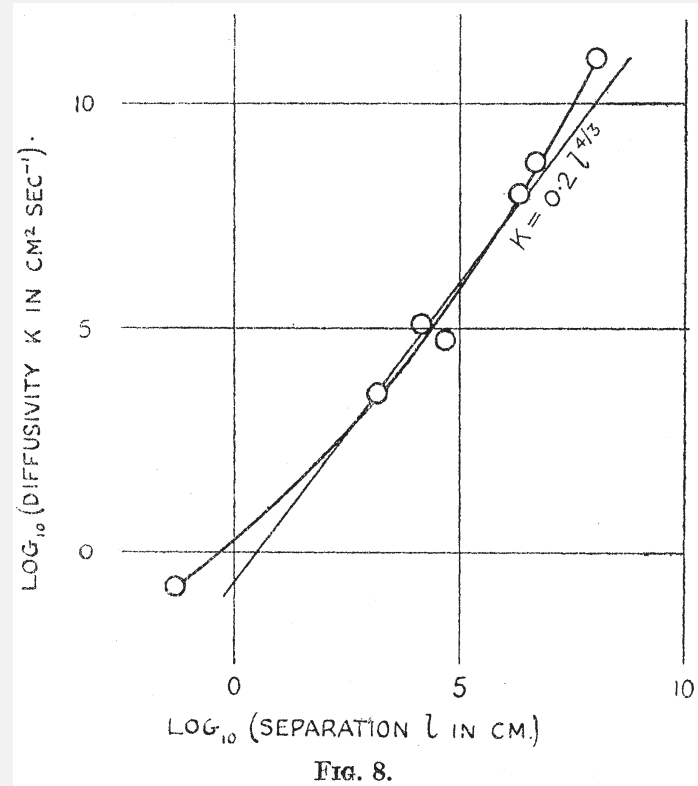


George Keith Batchelor

# Richardson (relative) diffusion in turbulence: $\langle l^2(t) \rangle \simeq t^3$



Brown  
Turbulent spreading

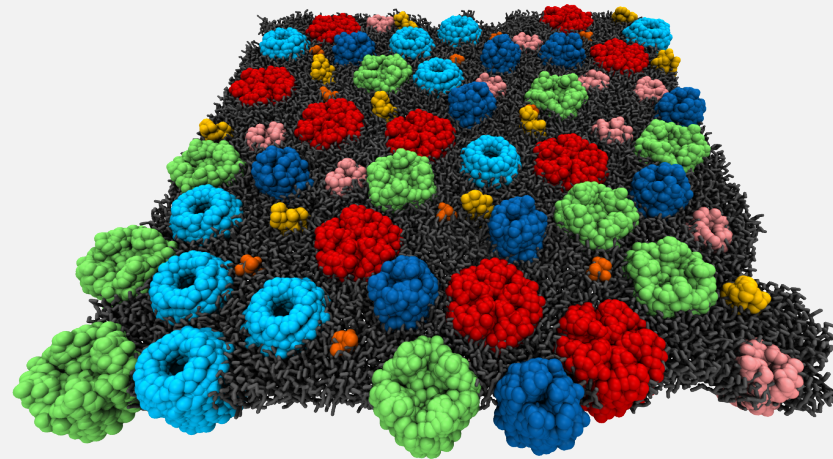
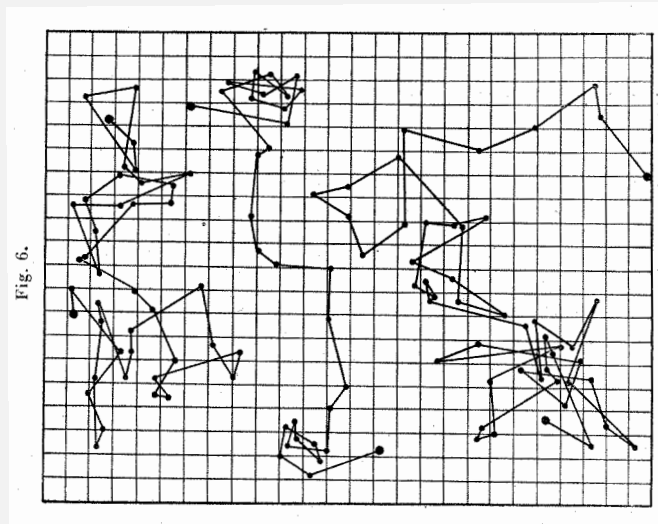


$$\frac{\partial q}{\partial t} = \varepsilon \frac{\partial}{\partial l} \left( l^{4/3} \frac{\partial q}{\partial l} \right), \quad \varepsilon \sim 0.4 \text{ cm}^{2/3} \text{ sec}^{-1} \quad \text{Richardson}$$

$$\frac{\partial q}{\partial t} = \bar{\varepsilon} t^2 \frac{\partial^2}{\partial l^2} q(l, t) \quad \text{Batchelor}$$

# Stochastic processes in 2018: why should we care?

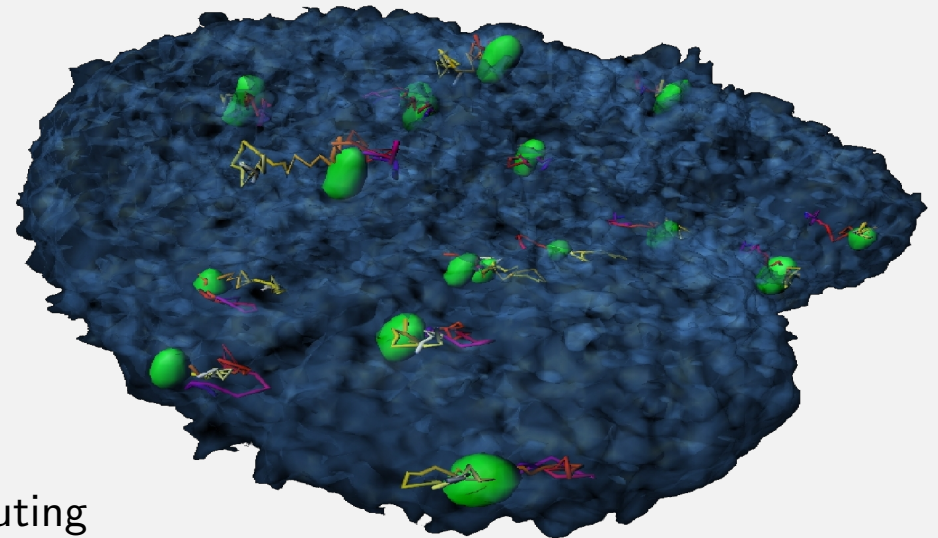
Jean Perrin (1908)



Courtesy Matti Javanainen

1905: Albert Einstein & Karl Pearson  
1906: Marian Smoluchowski  
1908: Paul Langevin  
1914: Ivar Nordlund  
1935: Eugen Kappler  
Later: Skorokhod, Lévy, Mandelbrot,  
Montroll, Weiss, Hänggi, etc.

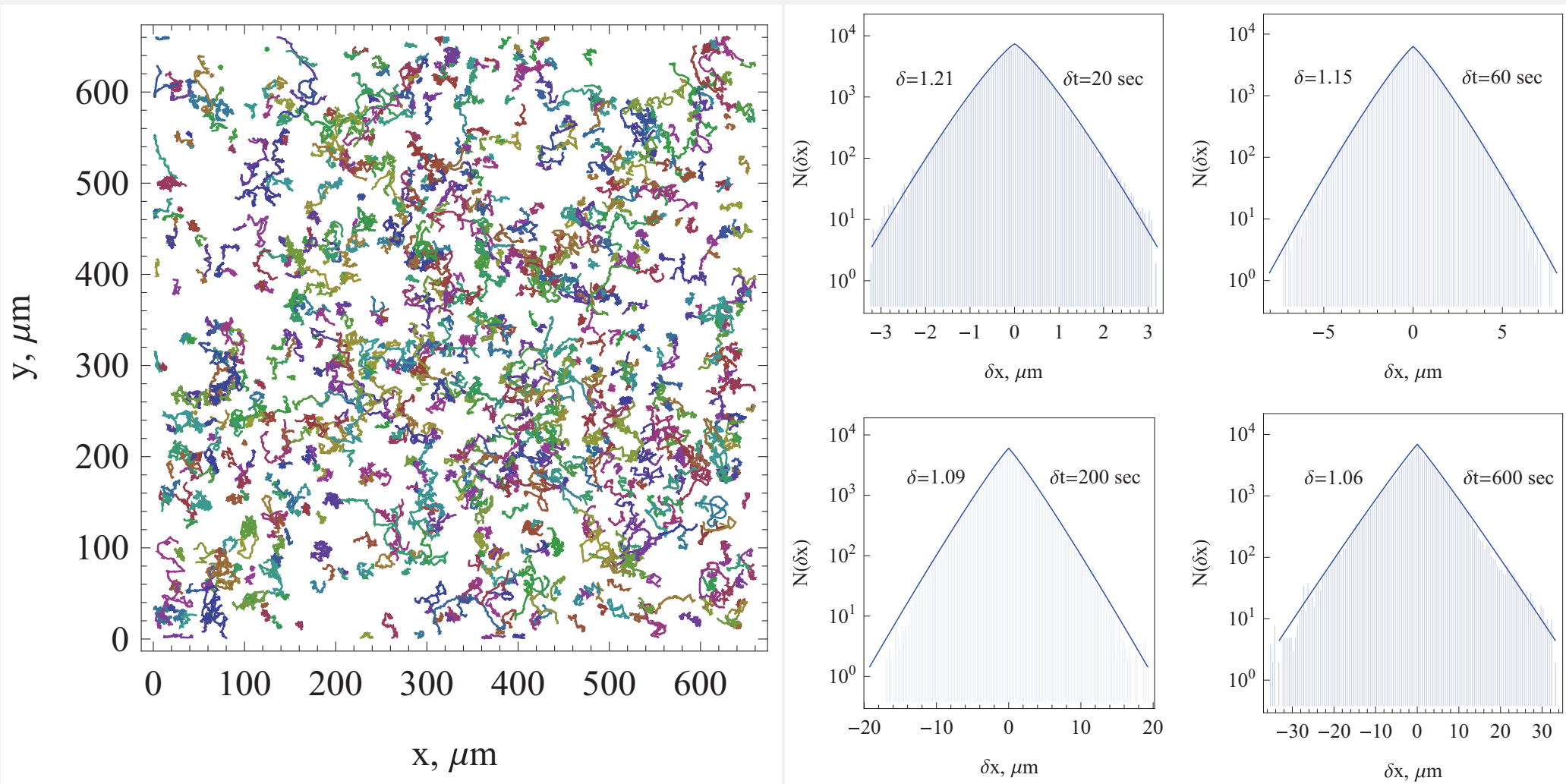
Now: superresolution microscopy & supercomputing  
>10<sup>6</sup> data points per trajectory, nm/sub-msec resolution



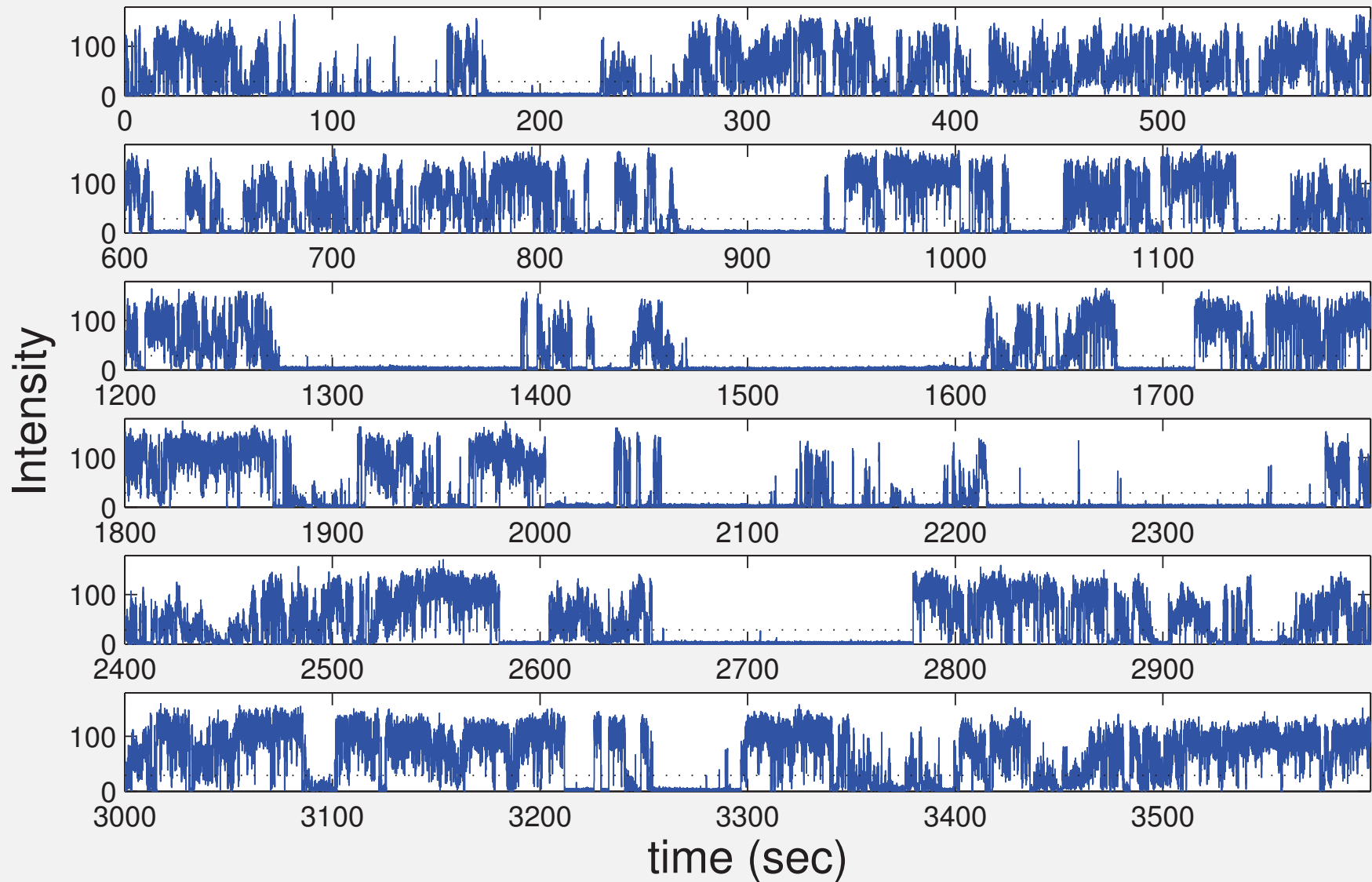
Courtesy Yuval Garini

E Barkai, Y Garini & RM, Phys Today (2012)

# Non-Gaussian diffusion of Dictyostelium cells

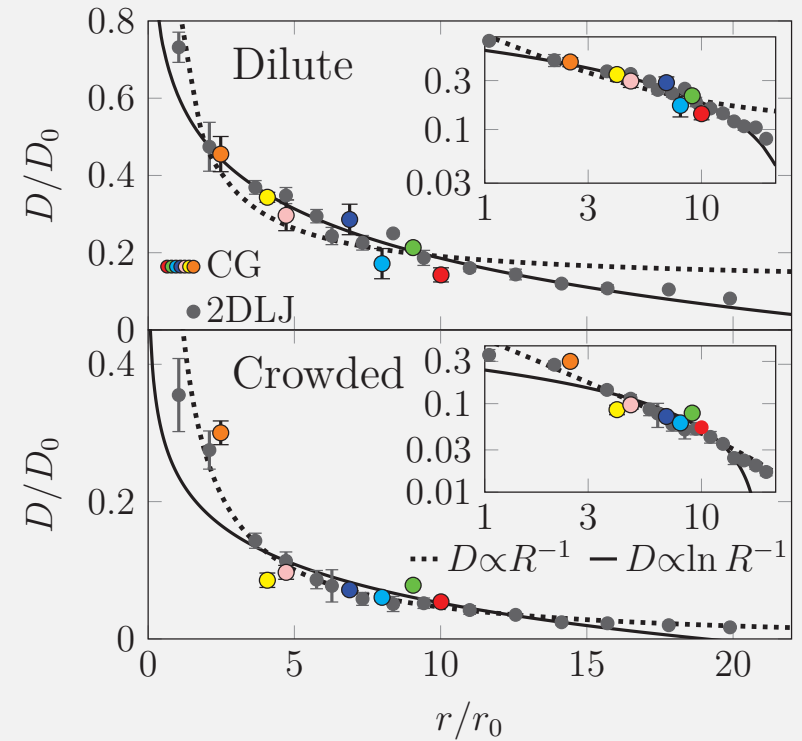
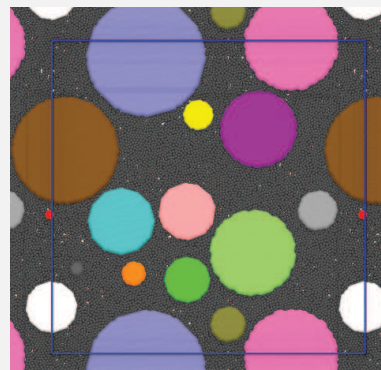
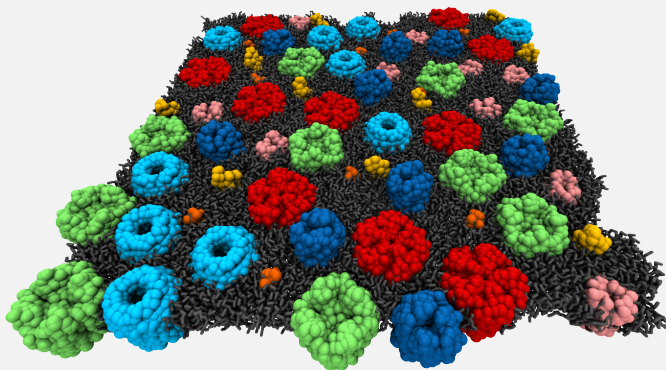
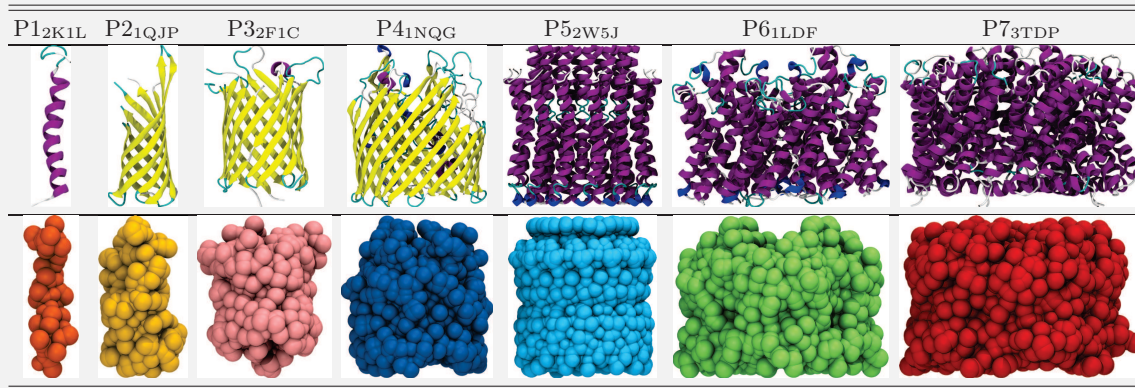


# On/off blinking dynamics in quantum dots





# Diffusion of proteins in crowded lipid bilayer membranes



Dilute system: Saffman-Delbrück law

$$D(R) \simeq \log(1/R)$$

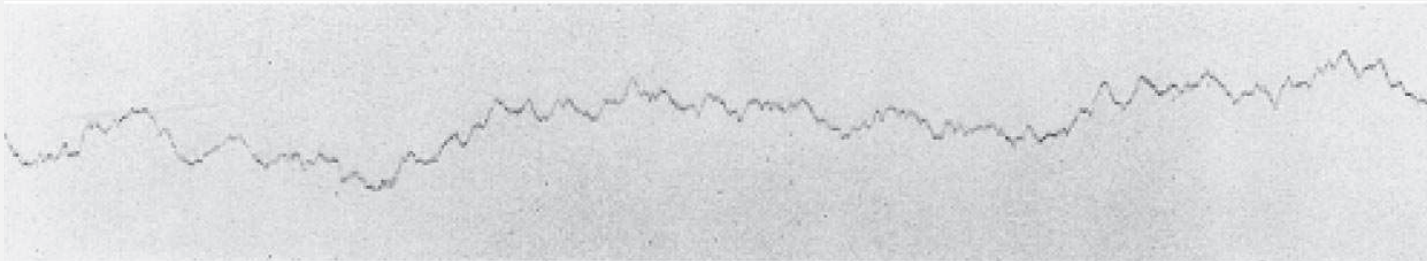
Crowded membrane & 2DLJ discs:

$$D(R) \simeq 1/R$$

# Anomalous diffusion, ensemble & time averaged MSD

Ensemble averaged MSD (subdiffusion:  $0 < \alpha < 1$ ; superdiffusion:  $1 < \alpha < 2$ ):

$$\langle \mathbf{r}^2(t) \rangle = \int \mathbf{r}^2 P(\mathbf{r}, t) d\mathbf{r} \simeq K_\alpha t^\alpha$$



E Kappler (1931)

Time averaged MSD:

$$\overline{\delta^2(\Delta)} = \frac{1}{T - \Delta} \int_0^{T-\Delta} [\mathbf{r}(t + \Delta) - \mathbf{r}(t)]^2 dt; \quad \langle \overline{\delta^2(\Delta)} \rangle = N^{-1} \sum_{i=1}^N \overline{\delta_i^2(\Delta)}$$

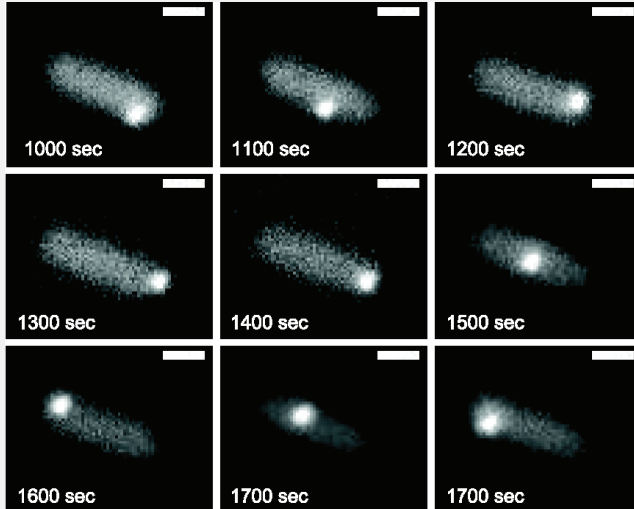
Ergodicity:

$$\langle \mathbf{r}^2(\Delta) \rangle = \lim_{T \rightarrow \infty} \overline{\delta^2(\Delta)}$$

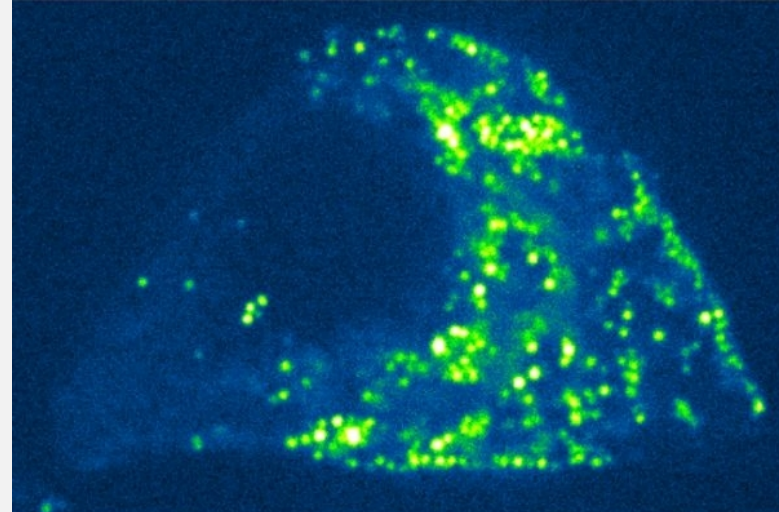
Ergodicity breaking parameter:  $\text{EB} = \langle \xi^2 \rangle - 1$  with  $\xi = \overline{\delta^2(\Delta)} / \langle \overline{\delta^2(\Delta)} \rangle$

Brownian motion:  $\text{EB} \simeq (\Delta/T)$

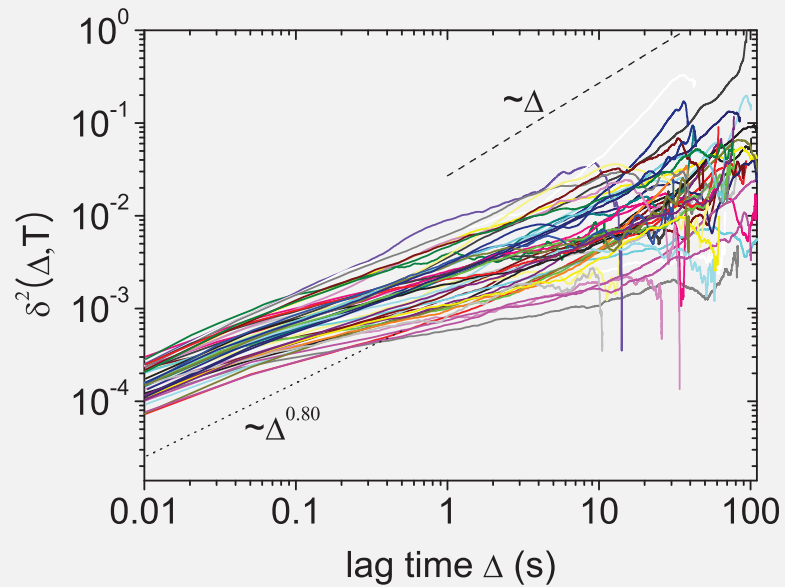
# In vivo anomalous diffusion of submicron tracers: $\langle r^2(t) \rangle \simeq t^\alpha$



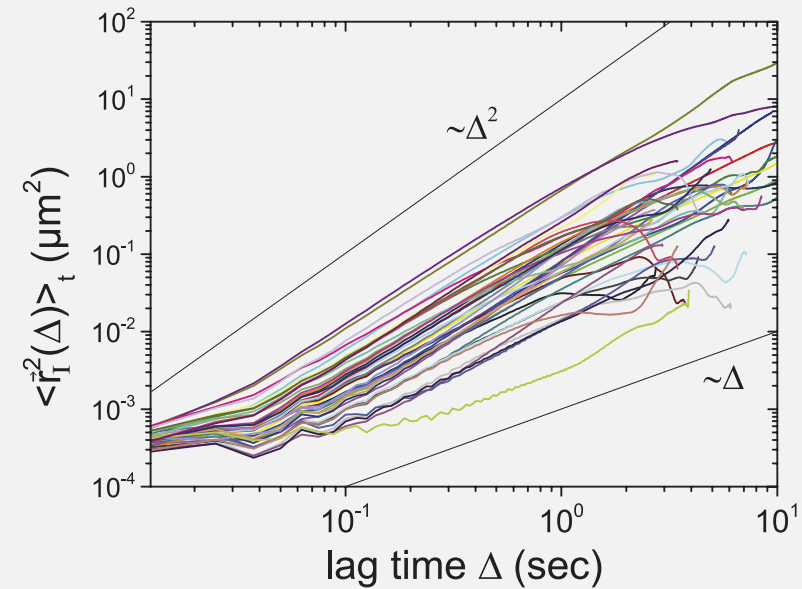
I Golding & EC Cox, PRL (2006)



SMA Tabei et al, PNAS (2013)

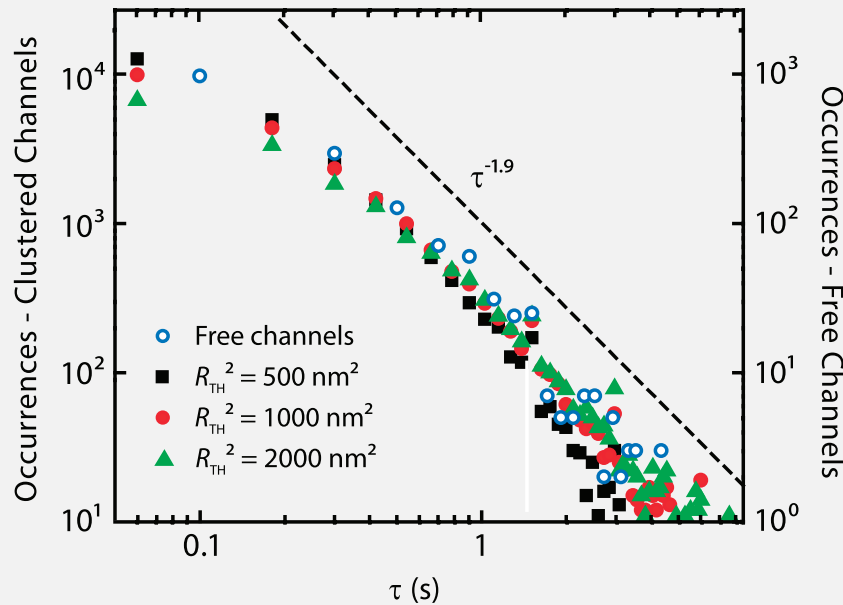
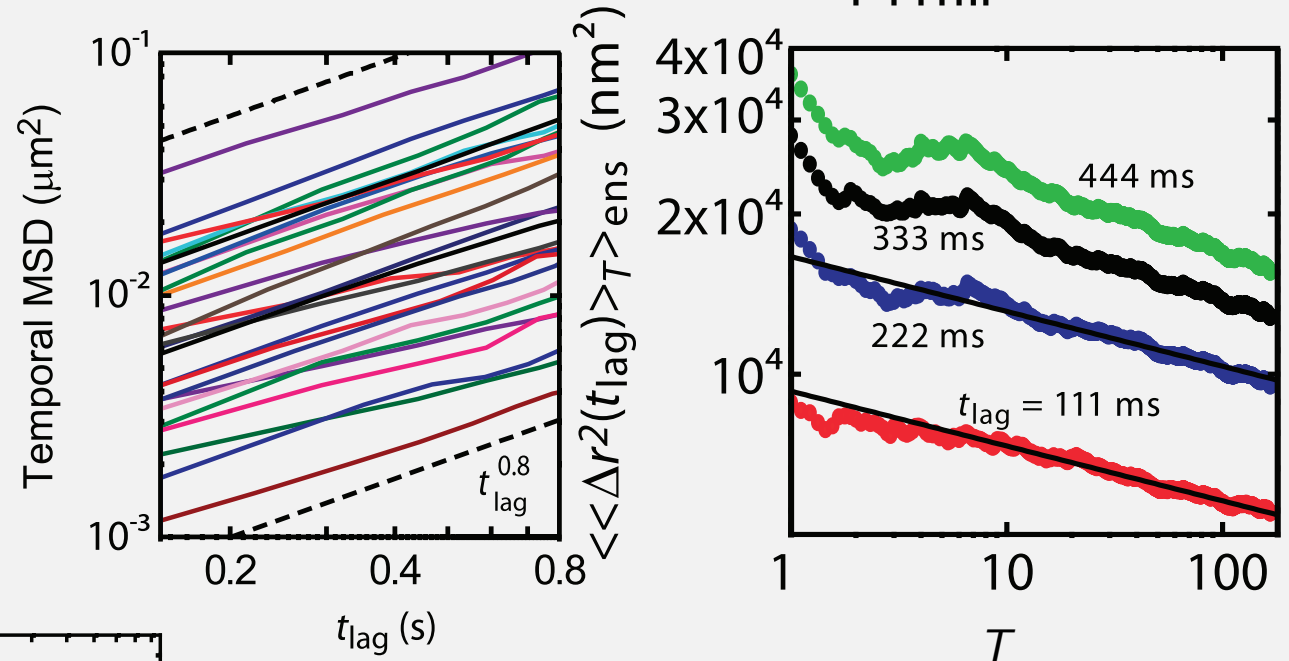
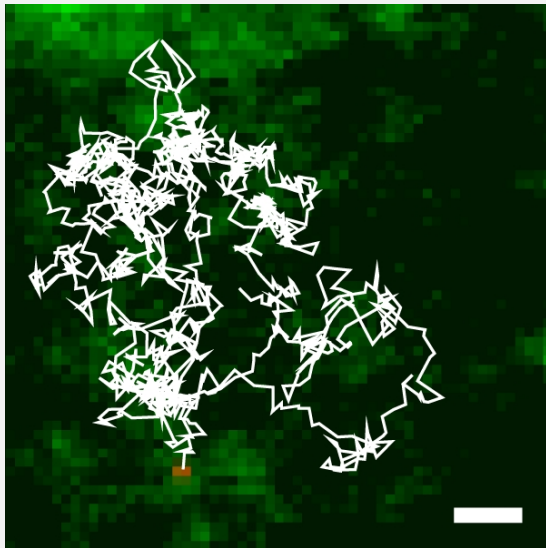


JH Jeon, . . . LB Oddershede & RM, PRL (2011)



J Revere, . . . RM & C Selhuber-Unkel, Sci Rep (2015)

# Ageing motion of Ka channels in plasma membrane

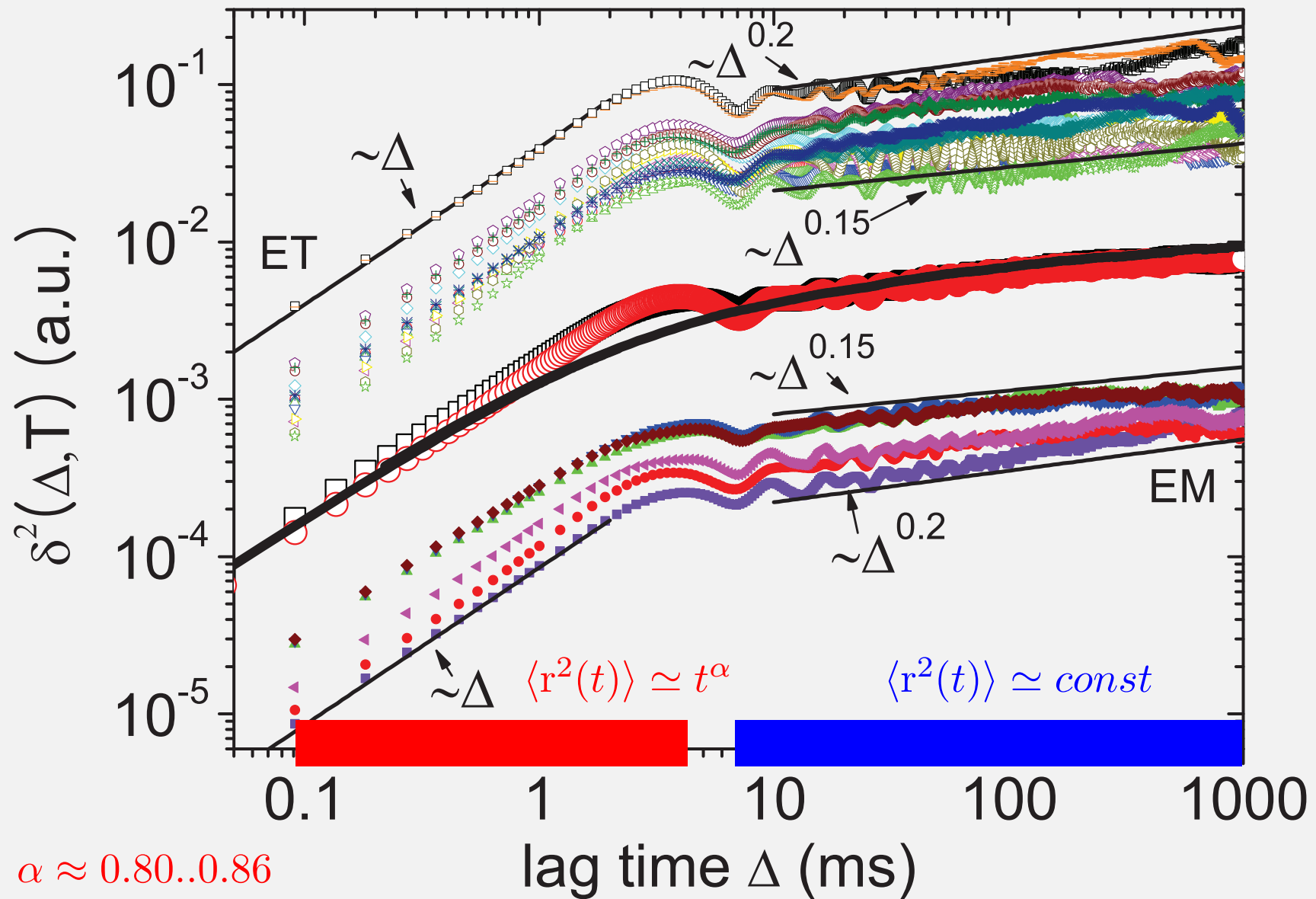


$$\psi(\tau) \simeq \tau^{-1-\alpha} \text{ scale free}$$

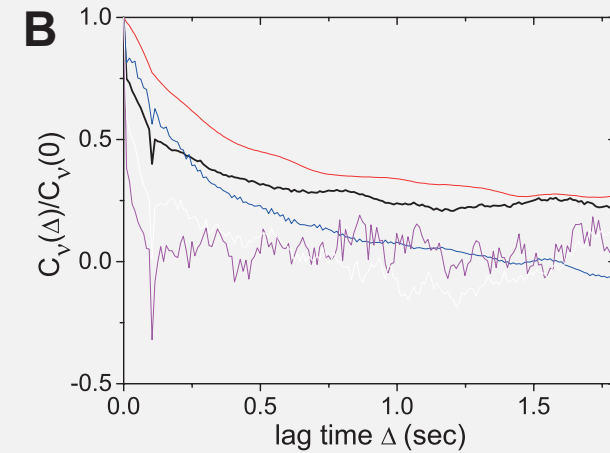
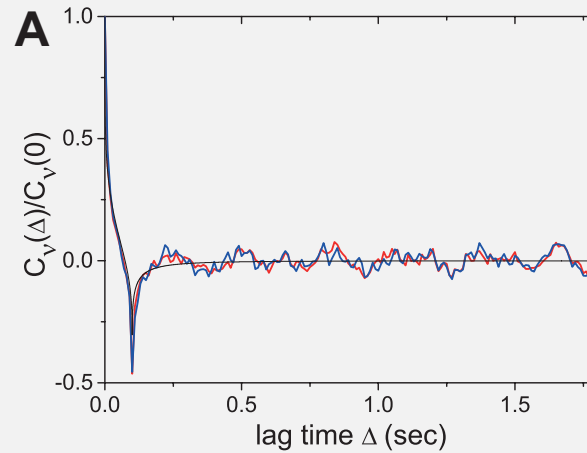
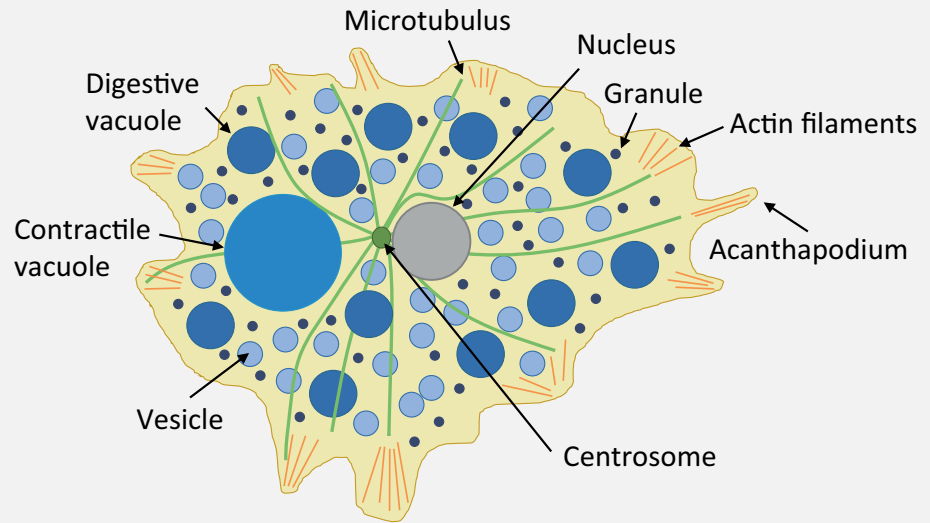
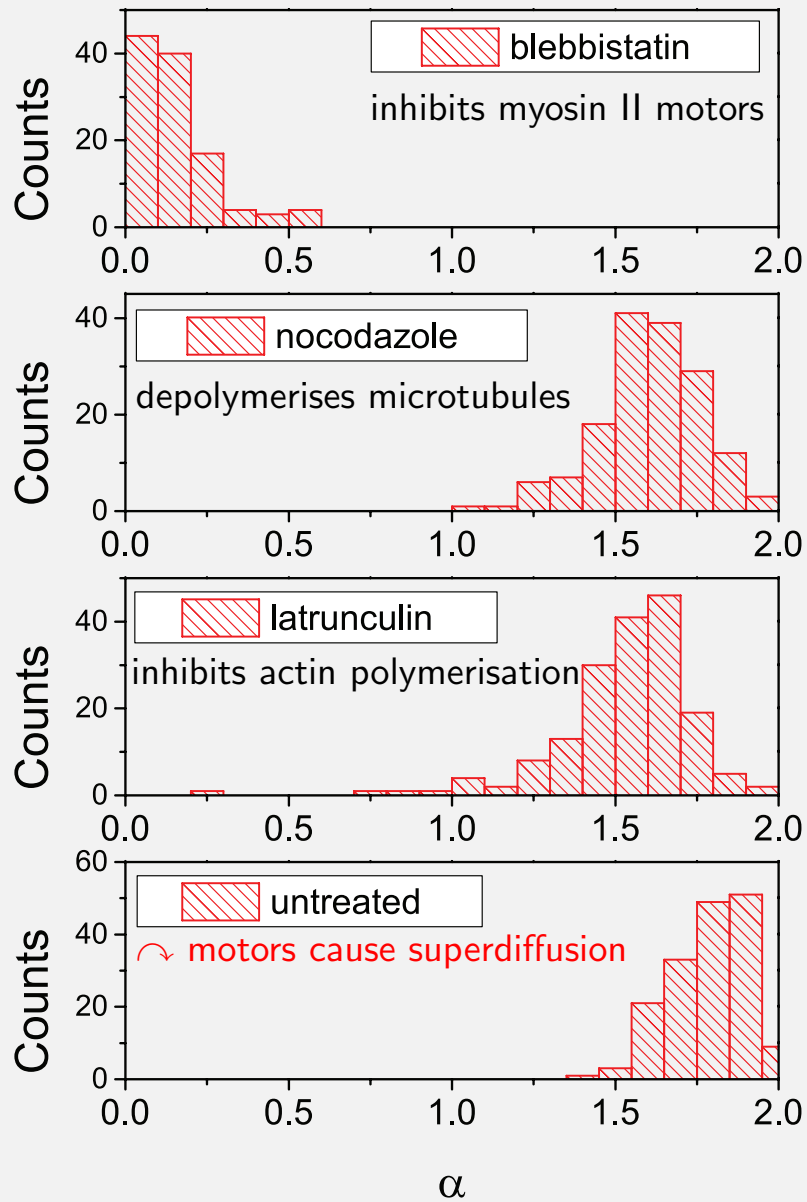
$$\overline{\delta^2(\Delta)} \text{ apparently random}$$

$$\overline{\delta^2(\Delta)} \neq \langle \mathbf{r}^2(\Delta) \rangle \text{ WEB}$$

# Granule subdiffusion in harmonic optical tweezer potential



# Superdiffusion in living *Acanthamoeba castellani*



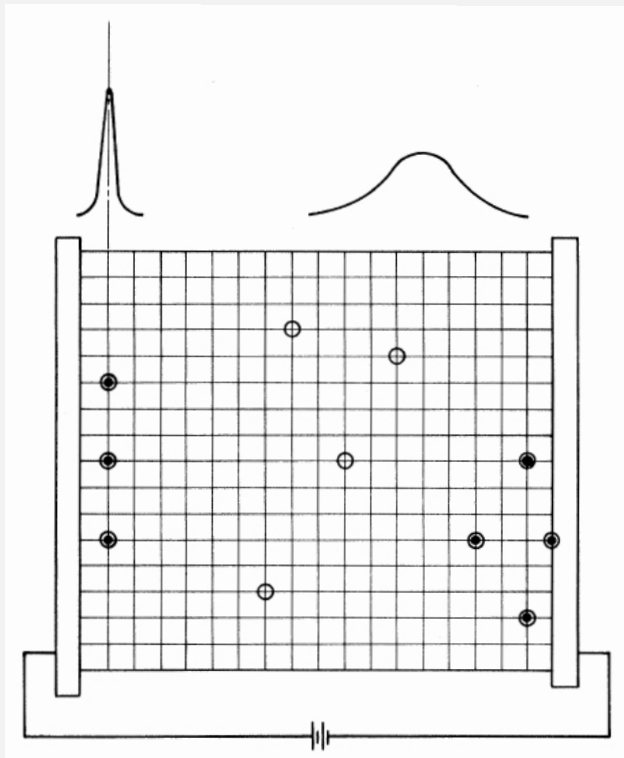
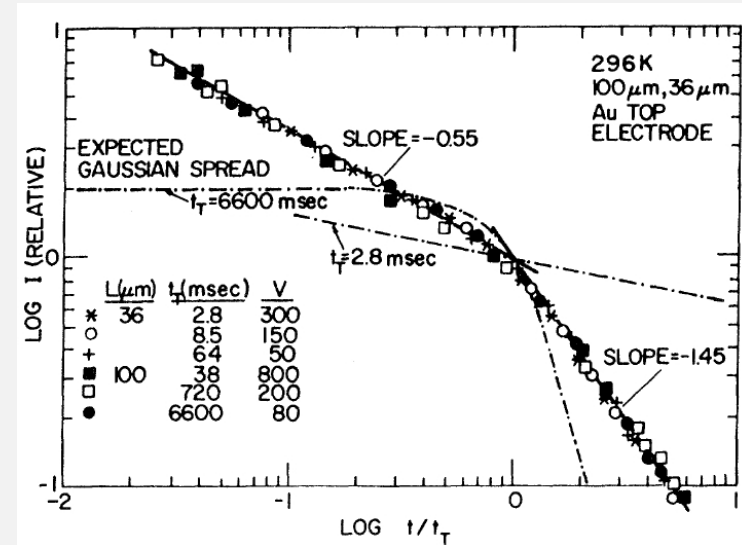
# Charge carrier diffusion in amorphous semiconductors

Waiting time distribution

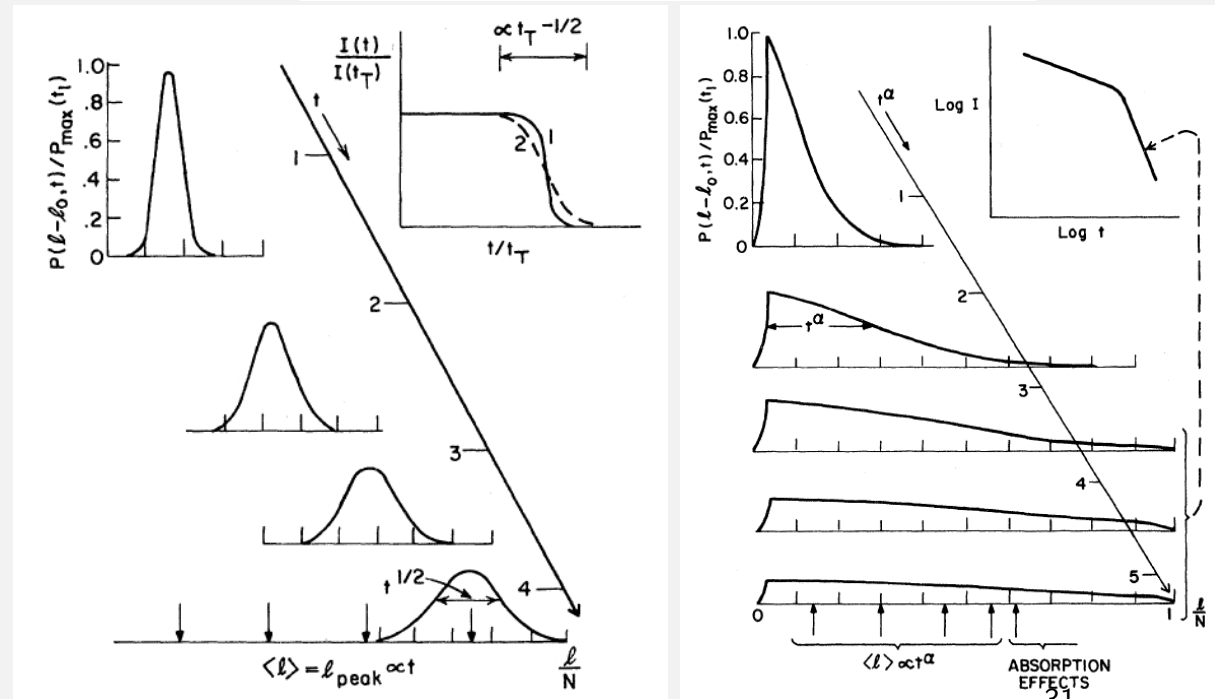
$$\psi(t) \simeq \frac{\tau^\alpha}{t^{1+\alpha}} \Leftrightarrow \psi(u) = \exp(-[u\tau]^\alpha)$$

In the bias of the electrical field:

$$\frac{\sqrt{\langle(\Delta x)^2\rangle}}{\langle x(t)\rangle} \simeq t^0 \iff \underbrace{\frac{\sqrt{\langle(\Delta x)^2\rangle}}{\langle x(t)\rangle}}_{\alpha=1} \simeq t^{-1/2}$$

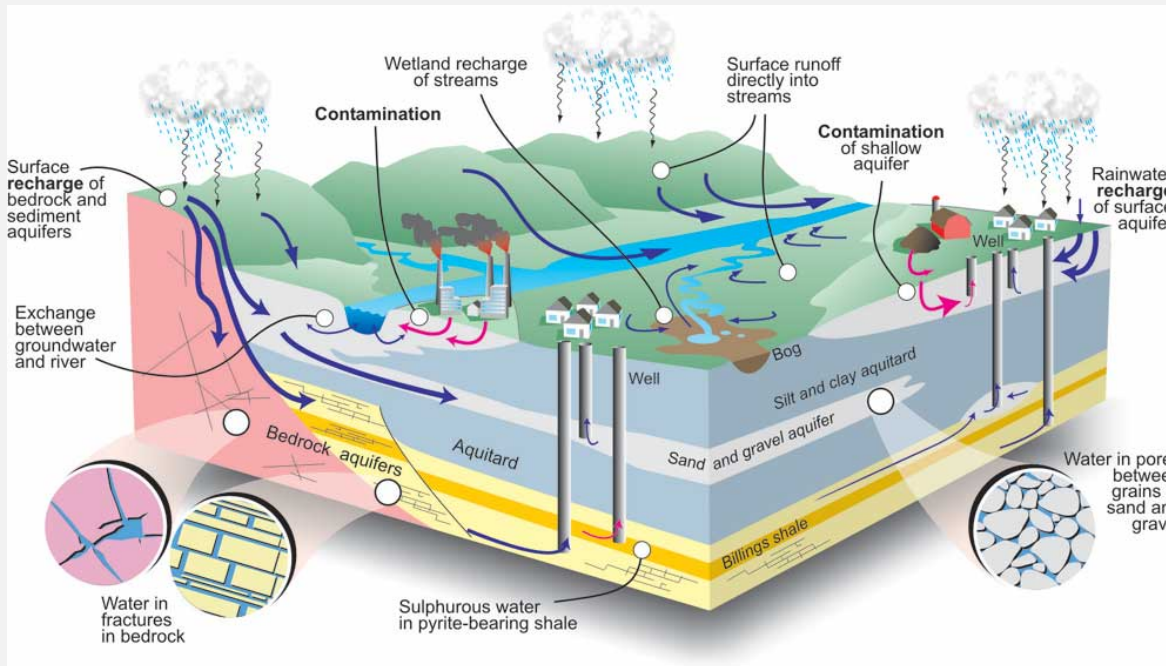


H Scher & E Montroll, PRB (1975)

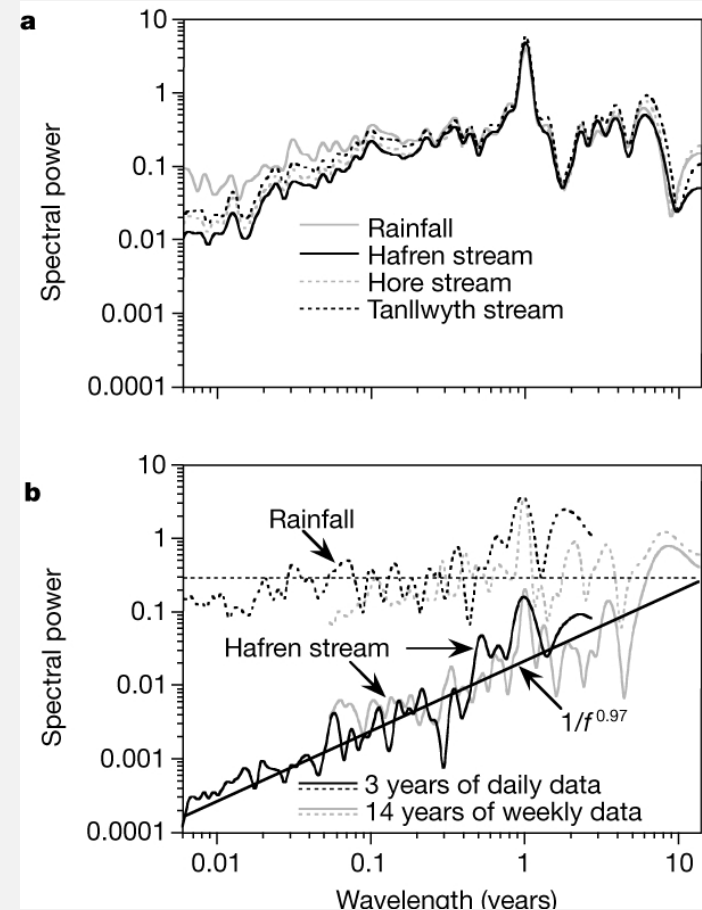


# Subsurface hydrology

Geoscape Ottawa-Gatineau

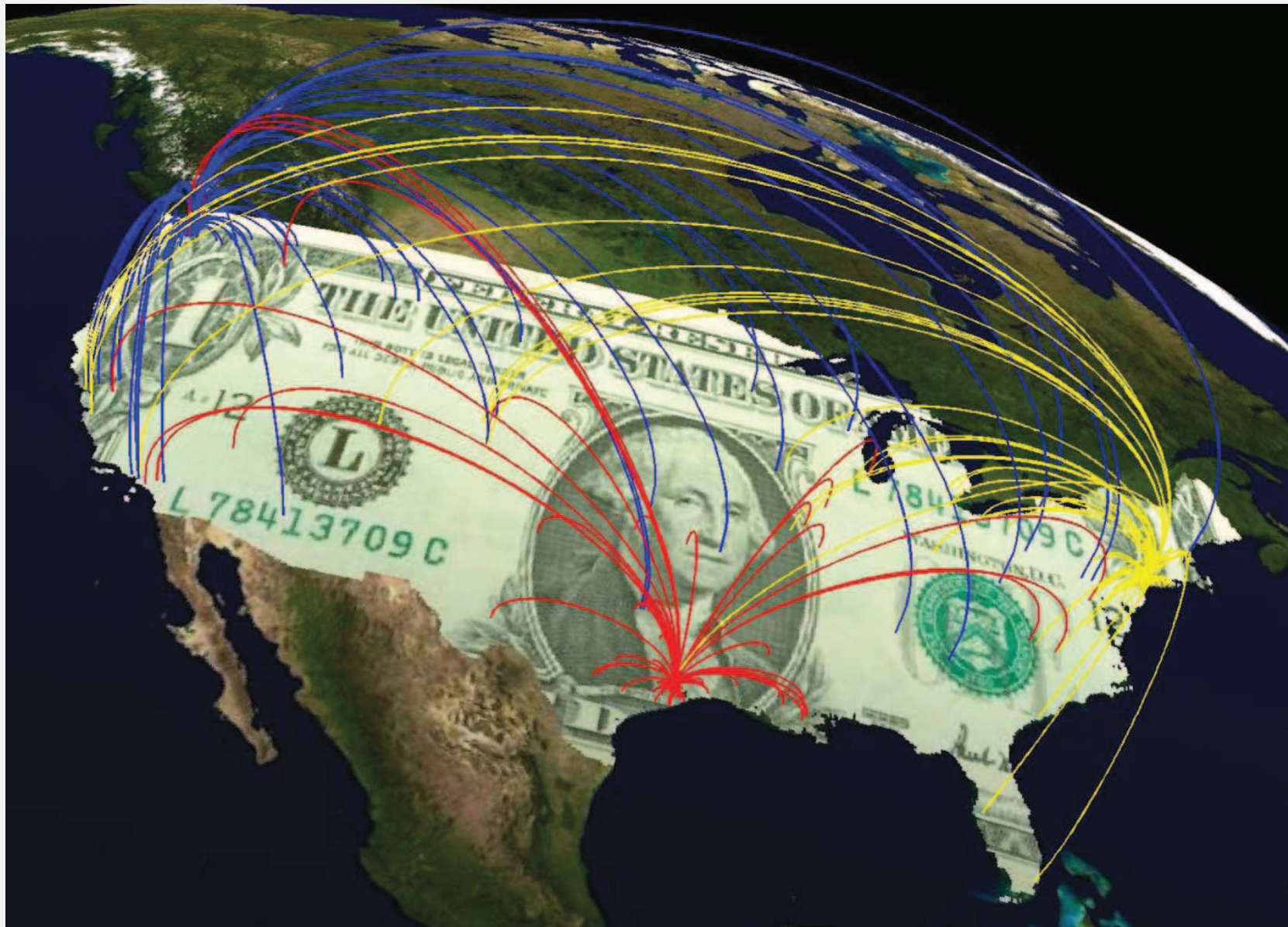


Contaminant transport in catchments

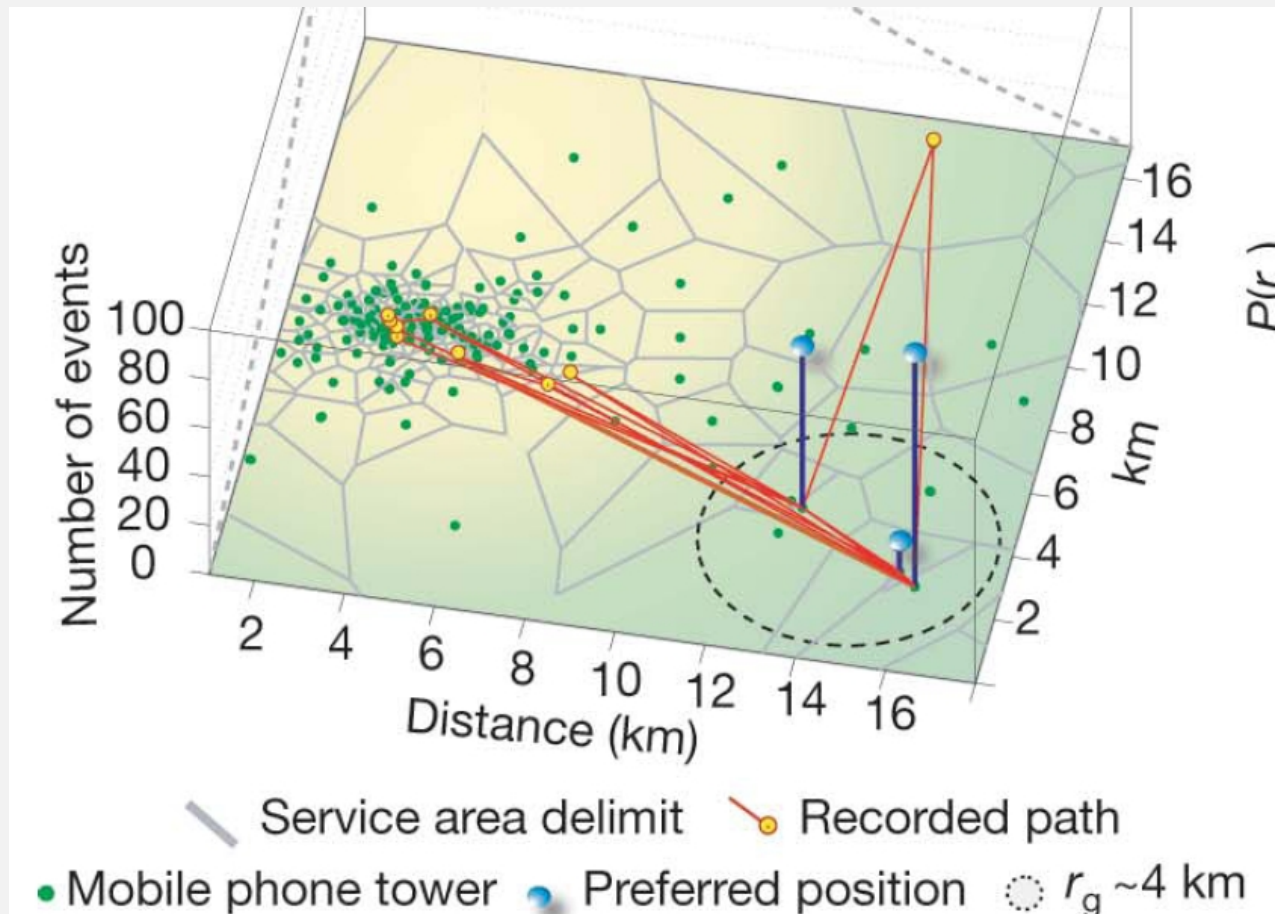




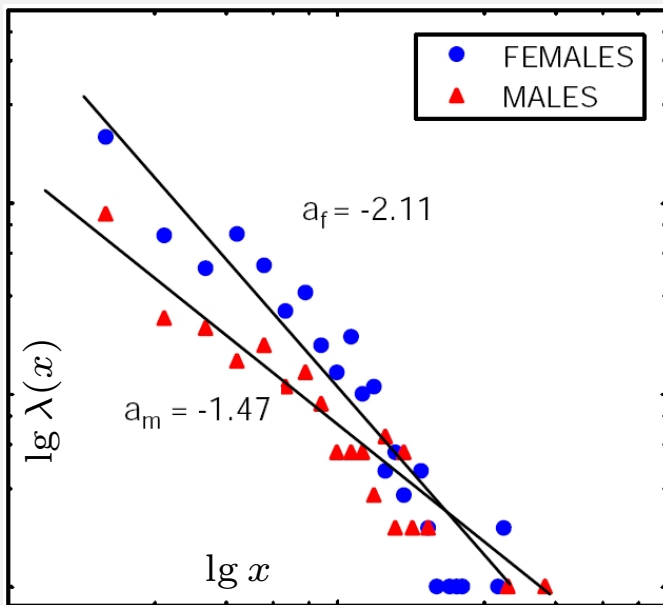
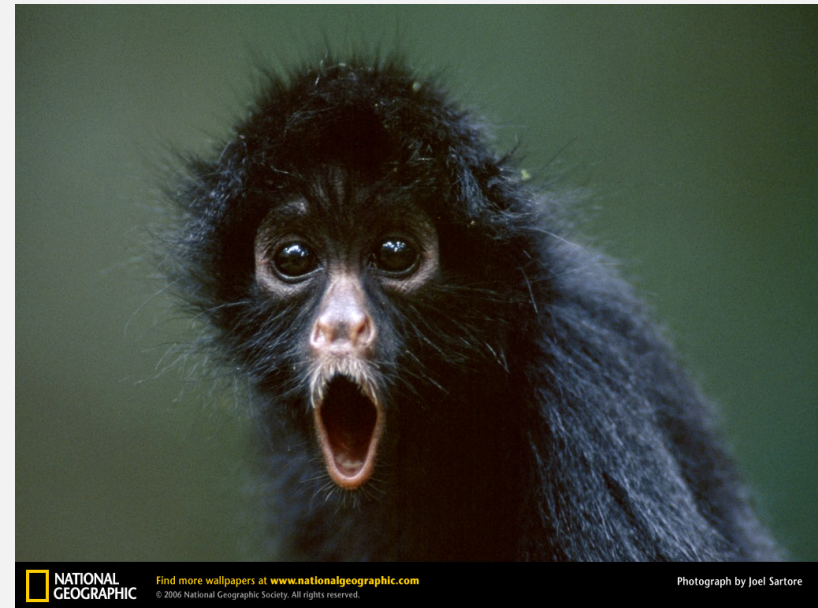
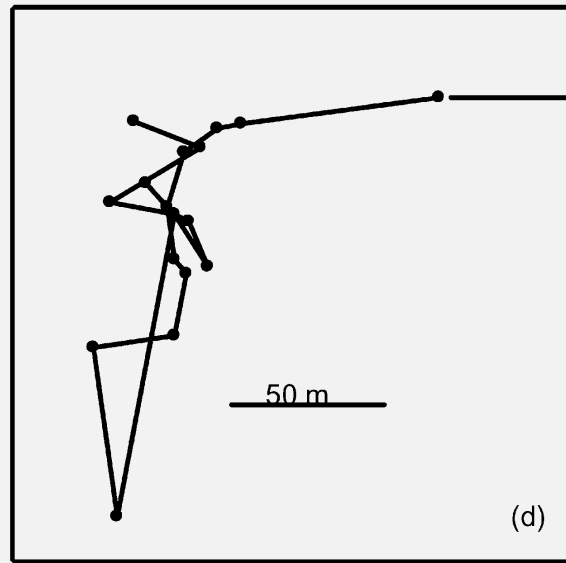
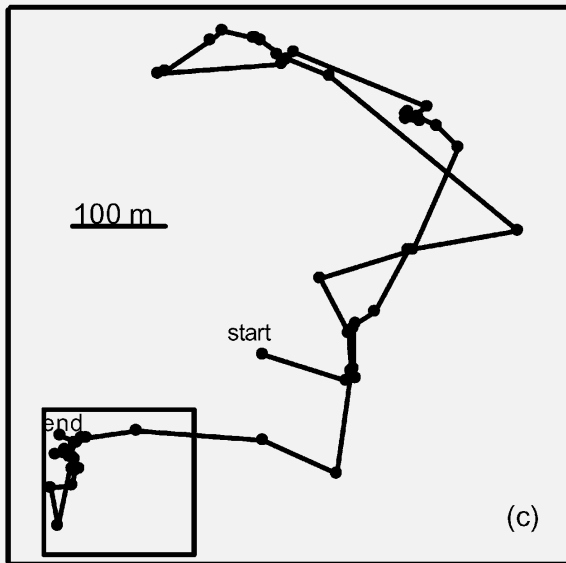
# The trace of money ...



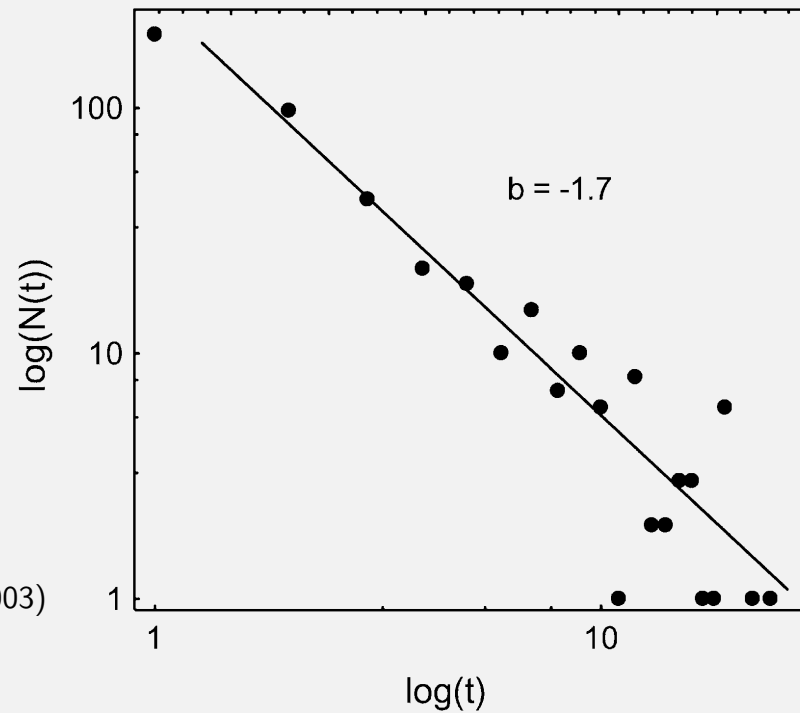
# Single human motion patterns: mobile phone tracking



# The jumps of the spider monkeys



Ramos-Fernandez et al, Behav Ecol Sociobiol (2003)



## Overview articles

I Single particle manipulation & tracking:

C Nørregaard, RM, CM Ritter, K Berg-Sørensen & LB Oddershede, Chem Rev **117**, 4342 (2017)

II Anomalous diffusion models, WEB & ageing:

RM, JH Jeon, AG Cherstvy & E Barkai, Phys Chem Chem Phys **16**, 24128 (2014)

III Ageing renewal theory:

JHP Schulz, E Barkai & RM, Phys Rev X **4**, 011028 (2014)

IIII Anomalous diffusion in membranes:

RM, JH Jeon & AG Cherstvy, Biochimica et Biophysica Acta - Biomembranes **1858**, 2451 (2016)

IIII Polymer translocation:

V Palyulin, T Ala-Nissila & RM, Soft Matter **10**, 9016 (2014)